

CLAIMS

1. Polymerizable composition for making episulfide based resins comprising :

- 5 A) at least one episulfide compound bearing at least one episulfide and at least one functional group capable of polymerizing with episulfide groups, and
- B) an effective amount of a polymerization catalyst system comprising :
- 10 - at least one salt of formula



wherein

- 15 M^{p+} is a cation selected from the group consisting of alkaline metals, alkaline earth metals, transitions metals and ammonium groups of formula NR_4^+ in which R is an alkyl radical,

Y^- is an anion such as the corresponding acid YH has a pKa fulfilling the condition $0.5 \leq pKa \leq 14$ with the proviso that when M^{p+} is an ammonium group, the catalyst system further comprises an electro-donor compound,

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P is the valency of the cation,

$n = mxp$, and

- at least one tertiary amine.

- 25 2. Polymerizable composition according to claim 1, wherein the associated acid YH has a pKa fulfilling the condition $0.5 \leq pKa \leq 8$.

 3. Polymerizable composition according to claim 1, wherein Y^- is selected from the group consisting of thiocyanate, carboxylate, thiocarboxylate, RS^- wherein R is a substituted or non-substituted alkyl group or phenyl group, acetylacetonate, diketone, acetoacetic ester, malonic ester, cyanoacetic ester, and ketonitrile.

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 4. Polymerizable composition according to claim 1, wherein the cation M^{p+} is selected from the group consisting of Li^+ , Na^+ , K^+ , Rb^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} and Al^{3+}

5. Polymerizable composition according to claim 1, wherein the salt is KSCN.

6. Polymerizable composition according to claim 1, wherein the salt is present in amount of 0.001 to 2.5%, based on the total weight of the polymerizable monomers present in the composition.

7. Polymerizable composition according to claim 6, wherein the salt is present in an amount of 0.001 to 1% based on the total weight of the polymerizable monomers present in the composition.

8. Polymerizable composition according to claim 1, wherein the tertiary amine has formula :



in which the R groups represent, independently from each other, an alkyl radical, a cycloalkyl radical or mixtures thereof.

9. Polymerizable composition according to claim 1, wherein the tertiary amine is selected from N,N-dimethylcyclohexylamine, N,N-dicyclohexylmethanamine and mixtures thereof.

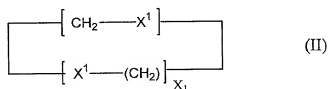
10. Polymerizable composition according to claim 1, wherein the tertiary amine is present in the composition from 0.05 to 5%, based to the total weight of the polymerizable monomers present in the composition.

11. Polymerizable composition according to claim 10, wherein the tertiary amine is present from 0.05 to 2%.

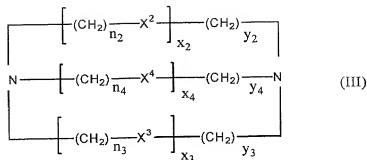
12. Polymerizable composition according to claim 1, further comprising an electro-donor compound enhancing the reactivity of the polymerization reaction.

13. Composition according to claim 12, wherein the electrodonor compound is selected from the group consisting of acetonitrile compounds, amide compounds, sulfones and sulfoxides, trialkylphosphites, nitro compounds, ethyleneglycol ethers, crown ethers and kryptates.

14. Composition according to claim 13, wherein the crown ethers and the kryptates are selected from the compounds of formulae :



and



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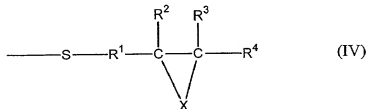
wherein X^1 represents O, S or NH, x_1 is an integer from 3 to 6,

X^2 , X^3 and X^4 represent O or S, n_2 , n_3 , n_4 , y_2 , y_3 , y_4 are 2 or 3, and x_2 , x_3 , x_4 are 2 or 3.

15. Composition according to claim 13, wherein the electro-donor compound represents up to 5% by weight of the total weight of the polymerizable monomers present in the composition.

16. The composition of claim 1, wherein the episulfide monomer comprises one or more episulfide structure of formula :

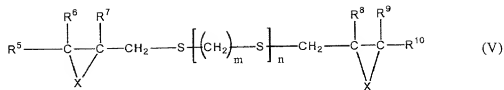
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20 in which R^1 represents a hydrocarbon group having 1 to 10 carbon atoms, R^2 , R^3 and R^4 each represents an hydrogen atom or a hydrocarbon group having 1 to 10 carbon atoms, X represents S or O with the proviso that in the molecule the average number of S represented by X is about 50% of the total number of S and O constituting the three membered ring.

17. Composition of claim 1, wherein the episulfide monomer is a compound of formula :

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in which R⁵, R⁶, R⁷, R⁸, R⁹ and R¹⁰ each represents an hydrogen atom or a hydrocarbon group having 1 to 10 carbon atoms, X represents S or O with the proviso that, in the molecule, the average number of S represented by X is about 50% or more of the total number of S and O constituting the three member rings, m represents an integer from 0 to 6 and n represents an integer from 0 to 4.

18. The composition of claim 17, wherein X is S.

19. The composition of claim 1, wherein the polymerizable monomers comprise solely episulfide monomers.

20. The composition according to claim 1, further comprising one or more polythiols of formula :

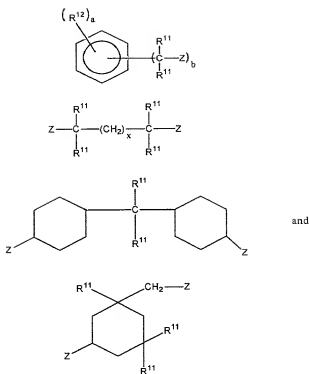


in which n' is an integer from 2 to 6 and R' is an organic group of valency equal to n'.

21. The composition according to claim 20, wherein the polythiol represents 0 to 30% by weight of the total weight of the polymerizable monomers present in the composition.

22. Composition according to claim 1, further comprising one or more polyiso(thio)cyanate monomers.

23. Composition according to claim 22, wherein the polyiso(thio)cyanate monomers are selected from the compounds having the formulae :



wherein :

- 5 R^{11} is independently H or C_1 - C_5 alkyl group,
 R^{12} is H, an halogen, or a C_1 - C_5 alkyl group,
 Z is $-N=C=O$ or $-N=C=S$;
 a is an integer ranging from 1 to 4, b is an integer ranging from 2 to 4
 and $a + b \leq 6$; and
- 10 x is an integer from 1 to 10.
24. Composition according to claim 23, wherein the
 polyiso(thio)cyanate monomers are selected from the group consisting of
 tolylene diiso(thio)cyanate, phenylene diiso(thio)cyanate, ethylphenylene
 diiso(thio)cyanate, isopropyl phenylene diiso(thio)cyanate,
 15 dimethylphenylene diiso(thio)cyanate, diethylphenylene diiso(thio)cyanate,
 diisopropylphenylene diiso(thio)cyanate, trimethylbenzyl triiso(thio)cyanate,
 xylylene diiso(thio)cyanate, benzyl triiso(thio)cyanate, 4,4'-diphenyl
 methane diiso(thio)cyanate, naphtalene diiso(thio)cyanate, isophorone
 diiso(thio)cyanate, bis(iso(thio)cyanate methyl) cyclohexane,
 20 hexamethylene diiso(thio)cyanate and dicyclohexylmethane
 diiso(thio)cyanate and mixtures thereof.

